a lower final iodine number. With Raney nickel alone at 125-150° we have not been able to reduce the iodine number of autoxidized methyl oleate below about 27. Even castor oil, in which the hydroxyl group is in the β-position to the double bond, behaved similarly. With the mixed catalysts iodine numbers of 5-7 (but not lower) are consistently obtained. Undoubtedly, a detailed study of hydrogenation conditions and catalysts would reveal the optimum technique, but we are presently studying the composition of the mixed hydroxy acids and do not intend to explore the hydrogenation reaction further.

To obtain hydroxyl oxygen contents of about 5% (calculated for monohydroxystearic acids, 5.3%) it is necessary to saponify the hydrogenation product. Some esters form during autoxidation and hydrogenation largely because of reaction between oxirane and carboxyl groups. The saponified product therefore should contain dihydroxystearic acid with contiguous hydroxyl groups. Analysis (24) of the final product indicates about 10% of α-glycols. Whether this arises exclusively from the oxirane ring-opening reaction or also from cyclic peroxide by reduction is not known. Earlier evidence suggests that the α-glycol is formed, at least in part, from cyclic peroxide (27).

Summary

Autoxidation of methyl oleate and oleic acid beyond the peak peroxide values followed by catalytic hydrogenation gave mixed monohydroxystearic acids in high yield. The complicated autoxidation mixture which contains peroxides, hydroxy, carbonyl, and oxirane compounds was simplified considerably in composition by this procedure.

For complete reduction of the double bond, and the carbonyl and oxirane groups, hydrogenation was conducted at about 150° and 150 lbs.. Peroxides were reduced at room temperature. Catalysts used were palladium on carbon and Raney nickel.

The selective reduction of peroxides in autoxidation mixtures has been studied by chemical and catalytic means. Peroxides were converted largely to carbonyl compounds rather than to the anticipated hydroxy compounds. Palladium-lead on calcium carbonate is an excellent catalyst for reducing peroxides with hydrogen.

tert-Butyl hydroperoxide, 12- ketostearic acid, stearone, *cis*-9,10-epoxystearic acid and methyl oleate peroxide concentrate were employed as model substances in determining hydrogenation conditions.

REFERENCES

1. Adkins, H., "Reactions of Hydrogen," pp. 12-14, The University of Wisconsin Press, (1937).
2. Adkins, H., and Billica, H. R., J. Am. Chem. Soc., *70*, 695-698 (1948).
3. Barnard, D., and Hargrave, K. R., Analyt. Chim. Acta, *5*, 476-488 (1951).
4. Coleman, J. E., Knight, H. B., and Swern, Daniel, J. Am. Chem. Soc., *74*, 4886-4889 (1952).
5. Coleman, J. E., Knight, H. B., and Swern, Daniel, J. Am. Oil Chemists' Soc., *32*, 135-137 (1955).
6. Ellis, G. W., Biochem. J., *26*, 791-800 (1932).
7. Ellis, G. W., Biochem. J., *30*, 753-761 (1936).
8. Ellis, G. W., Biochem. J., *46*, 129-141 (1950).
9. Ellis, G. W., J. Chem. Soc., *1950*, 9-12.
10. Farmer, E. H., and Sutton, D. A., J. Chem. Soc., *1943*, 119-122.
11. Farmer, E. H., and Sutton, D. A., J. Chem. Soc., *1946*, 10-13.
12. Findley, T. W., Swern, Daniel, and Scanlan, J. T., J. Am. Chem. Soc., 67, 412-414 (1945).
13. Holman, R. T., "Autoxidation of Fats and Related Substances," ch. II in vol. II of "Progress in the Chemistry of Fats and Other Lipids," published by Pergamon Press Ltd. (1954).
14. Knight, H. B., Coleman, J. E., and Swern, Daniel, J. Am. Oil Chemists' Soc., *28*, 498-501 (1951).
15. Knight, H. B., Eddy, C. R., and Swern, Daniel, J. Am. Oil Chemists' Soc., *28*, 188-192 (1951).
16. Knight, H. B., Jordan, E. F. Jr., Koos, R. E., and Swern, Daniel, J. Am. Oil Chemists' Soc., *31*, 93-96 (1954).
17. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, Daniel, Biochemical Preparations, *2*, 100-104 (1952).
18. Knight, H. B., and Swern, Daniel, J. Am. Oil Chemists' Soc., *26*, 366-370 (1949).
19. Lindlar, H., Helv. Chim. Acta., *35*, 446-450 (1952).
20. Mack, C. H., and Bickford, W. G., J. Org. Chem., *18*, 686-692 (1953).
21. Morris, S. G., J. Agr. Food. Chem., *2*, 126-132 (1954).
22. Mozingo, R., in Org. Syntheses, *26*, 77-82 (1946).
23. Pavlic, A. A., and Adkins, H., J. Am. Chem. Soc., *68*, 1471 (1946).
24. Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., Oil & Soap, *22*, 115-119 (1945).
25. Ross, J., Gebhart, A. I., and Gerecht, J. F., J. Am. Chem. Soc., *71*, 282-286 (1949).
26. Saunders, D. H., Ricciuti, C., and Swern, Daniel, J. Am. Oil Chemists' Soc., *32*, 79-83 (1955).
27. Swern, Daniel, Coleman, J. E., Knight, H. B., Ricciuti, C., Willits, C. O., and Eddy, C. R., J. Am. Chem. Soc., *75*, 3135-3137 (1953).
28. Swern, Daniel, Scanlan, J. T., and Knight, H. B., J. Am. Oil Chemists' Soc., *25*, 193-200 (1948).
29. Swift, C. E., Dollear, F. G., and O'Connor, R. T., Oil & Soap, *23*, 355-359 (1946).
30. Wilds, A. L., in "Organic Reactions," vol. II, ch. 5, John Wiley and Sons Inc., New York (1944).

Urea Adducts of Mono- and Diesters of Fatty Acids

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SOME OF THE USES for monoglycerides indicate that they should be free of di- and triglycerides and preferably contain unsaturated fatty acid esters (1, 2). The wide difference in molecular weights of mono- and diesters suggests a distillation process, but low vapor pressure and thermal instability make molecular distillation the only possible distillation method effective (1). The molecular distillation method reduces the amount of undesirable di- and triglycerides and produces a monoglyceride that contains 90-95% monoester. However the molecular distillation process has been of little value in fractionating soybean glycerides with respect to unsaturation. A spread of 12 units in iodine number (127-139) is the maximum reported (3). Kuhrt *et al.* (1) have obtained a 30% cut taken between 142-168°C. at .04 mm. pressure from a reaction product of a partially hydrogenated vegetable oil and glycerine that contained 94% monoesters. This cut represented 75% of the monoglycerides present. Although no commercial solvent extraction process is available at present to refine technical monoglycerides, Feuge and Gros (4) have purified a technical monoglyceride by distributing it between hexane and aqueous methanol or ethanol. They obtained a product from the ethyl alcohol layer that contained 70% of the monoglycerides in 80% purity. No evidence was given to show any degree of separation based on unsaturation.

It was the purpose of this work to determine what kind and degree of separation could be obtained by reacting crystalline solid urea with the fatty acid mono- and di-esters of glycerol. The 18 carbon nor-

mal chain of saturated fatty acid monoesters should form a fairly stable complex with urea. The *cis* double bond in oleic acid creates a kink in the chain of the fatty acid, reducing the ease and speed with which urea can form a complex with oleic esters. Linoleic acid with two *cis* double bonds departs farther from the linearity of stearic acid, and the three nonconjugated *cis* double bonds in linolenic acid make complex formation very difficult. Separations based on these differences have previously been used to extract saturated fatty acids of semi-drying oils (5, 6, 7, 8). Besides separating glycerol monoesters according to the amount of unsaturation of the acid part of the ester, it was thought that extraction with urea might offer a means to separate mono- from di- and triesters. The commercially available monoglycerides are normally made by reacting fats or fatty acids with glycerol in the presence of alkaline catalysts. The product of the reaction will contain from 40-60% monoglyceride and free glycerol, fatty acid, and di- and triglycerides and is often used without any further refinement to concentrate the monoester content.

It was desired in this study a) to increase the proportion of monoglyceride in the technical product and b) to obtain a fraction of monoester of greater degree of unsaturation. Since it was expected that monoesters would form urea adducts before diesters and saturated esters before unsaturated ones, the degree of selectivity or preferential formation was of interest. The study was divided into three parts: a) extraction of distilled monoglycerides of soybean and cottonseed oils to determine the degree of separation of saturated from unsaturated esters; b) extraction of mixtures of mono- and diglycerides of a saturated acid (lauric), where no separation on the basis of unsaturation can occur; c) extraction of mixtures of mono- and diglycerides where differences in both unsaturation and degree of esterification occur. In one case the mixture was of distilled mono- and diglycerides of cottonseed fatty acids, where the proportion of mono- and diglycerides was accurately known. In the other case technical mono-oleate, containing substantial amounts of diesters, was used.

Experimental

Materials. Cottonseed oil monoglycerides (Myverol 18-85, Sap. No. 159, I.V. 94), cottonseed oil diglycerides (D-45105-2, Sap. No. 183 I.V. 97), and soybean oil monoglycerides (MVG-3-79, Sap. No. 154 I.V. 109) were obtained from Distillation Products Industries, Eastman Kodak Company. They are distilled esters containing no catalyst and a maximum of 1% glycerol and 1.5% free fatty acids. Technical glycerol monooleate (S-1096) and glycerol monolaurate (S-1062) used in the urea extractions were obtained from the Glyco Products Company. The technical monoesters were washed with a 20% solution of sodium sulfate to remove free glycerol; otherwise the mono- and diesters were used as received.

Procedure. Extractions of the glyceride mixtures were made by ball-milling a methyl isobutyl ketone solution of the different glyceride products with crystalline urea. The following extraction is typical of those made. A total of 50 g. of monoglycerides dissolved in 300 g. of methyl isobutyl ketone was weighed into a quart tin can with a friction cap lid. A volume of stone balls, enough to fill a 250-cc. beaker along with a weighed amount of crystalline urea, was added to the can. The can was then sealed and placed on moving rolls. The ball-milling continued overnight at ambient room temperature for approximately 16 hrs. At the end of the ball-milling the crystalline adduct was filtered and washed with 200 cc. of methyl isobuytl ketone. The monoglycerides remaining in the filtrate after removal of the adduct were recovered solvent-free by distilling off the methyl isobutyl ketone under 1 mm. of pressure. The urea complex was decomposed by dissolving the urea in water and taking up the monoglyceride layer in methyl isobutyl ketone. The extract layer was washed with two portions of 100 cc. of warm water and dried with anhydrous magnesium sulfate; the extracted fraction of monoglyceride was recovered solvent-free by vacuum stripping the solvent at 1 mm. pressure.

Discussion

Urea Extraction of Cottonseed Oil Monoglyceride. Fifty g. of distilled cottonseed monoglyceride (saponification number 159, iodine number 94), dissolved in 300 g. of methyl isobutyl ketone, were extracted with three different amounts of urea. The composition of the extract and raffinate from each extraction was estimated by iodine number and saponification number. Iodine and saponification numbers of glycerol monooleate, which makes up approximately 33% of the cottonseed monoesters, are 76 and 157 and, of glycerol monolinoleate, which makes up approximately 44%, are 144 and 158. Glycerol monopalmitate, which makes up approximately 21% of the cottonseed monoesters, has a saponification number of 170.

Iodine number of the 8.91 g., or 18% extracted by 20 g. of urea, was 23, saponification number 166. This would indicate that it was composed of approximately 30% glycerol mono-oleate and 70% saturated monoglycerides. Iodine and saponification numbers of the raffinate from the first extraction were 106 and 152. The iodine number indicated that the raffinate fraction was composed of approximately equal parts of glycerol mono-oleate and monolinoleate and a small amount of saturated monoesters.

Iodine number of the 16.10 g. or 32% extracted by 42 g. of urea was 33, saponification number 166. This would indicate that the extract was composed of approximately 40% glycerol mono-oleate and 60% saturated monoesters. Iodine and saponification numbers of the raffinate for this second extraction were 118 and 159. These values indicate that the raffinate was composed of approximately 40% glycerol monooleate and 60% glycerol monolinoleate and a small amount of saturated monoesters.

The 125 g. of urea used in the third extraction were sufficient to form a complex with 40 g. of monoester in the extraction batch. Actually it formed a complex with only 23.86 g., or 48% of the monoester, in the sample. Iodine number of the 23.86 g. extracted was 45; saponification number was 163. These values would indicate that the extract was made up of approximately 50% mono-oleate ester, 45% monosaturated esters, and a small amount of monolinoleate ester. The raffinate from this third extraction had an iodine number and saponification number of 131 and 155, which indicated it was composed of approximately 15 to 20% mono-oleate and 80-85% glycerol monolinoleate ester.

The data from the three extractions are plotted graphically in Figures 1A, 1B, and 1C. Figure 1A

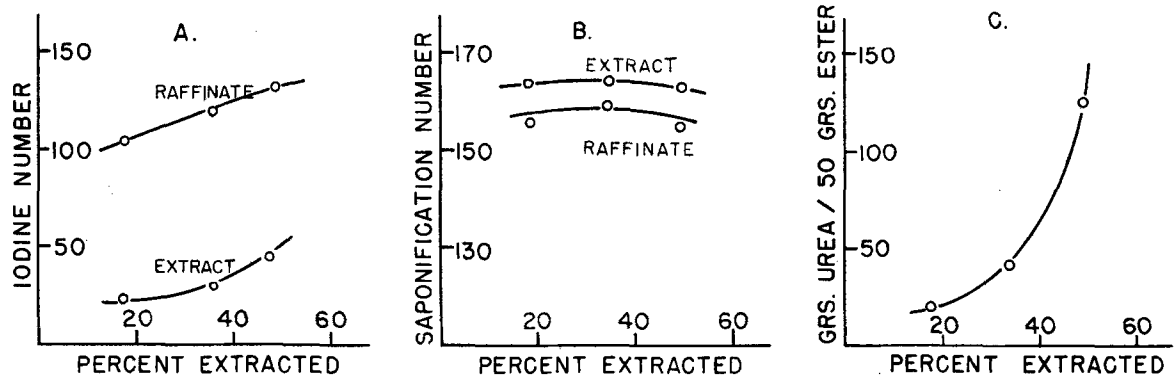

FIG. 1. Urea extraction of glycerol monoester of cottonseed oil fatty acids (saponification number 159, iodine number 94).

shows how iodine number of extract and raffinate varies as the amount extracted increases. Iodine numbers of extract and raffinate increase as the amount extracted increases. The first extraction removes most of the saturated esters, leaving oleate and linoleate esters in the raffinate. Further extraction will remove more saturated and some oleate esters, raising the iodine number of the extract and also, since the proportion of linoleate in the raffinate is higher, raising its iodine number also. Iodine number of the extract and raffinate at 18% extraction was 23 and 106, at 32% extraction was 33 and 118, and at 48% extraction was 45 and 131. In each extraction the spread in iodine number was about 85 points. The change in saponification number is not significant except to indicate how the palmitic acid monoglyceride is distributed between the extract and the raffinate. The saponification number of glycerol monopalmitate is 170 and that of stearic, oleic, and linoleic acids is 157, 157, and 158, respectively. Saponification number of the extract is 7-14 points higher than that of the raffinate, indicating that the monopalmitate is easily extracted by urea.

Figures 4, 5, and 6 are photographs of the Fisher-Hershfelder-Taylor atom models of glycerol monostearate, mono-oleate, and monolinoleate. The size and valence angles of the models are proportional to those of the atoms in the molecule. It is not possible to show the infinite positions which the free rotating bonds can assume. The glycerol monostearate in Figure 4 is linear except for the –OH on the glycerol part of the ester. The glycerol mono-oleate shown in Figure 5 is not as linear as the saturated monoester, but it does fit into the canal or central lumen of the urea spiral. The fit is tighter, with the result that the stability of the urea-mono-oleate complex is less than that of the glycerol monostearate complex. The fact that only 48% of the cottonseed monoesters would form a complex with urea even though an excess of urea were used and that iodine numbers of this fraction correspond to a composition of mostly saturated and oleate monoesters indicate that the two *cis* double bonds in the 9 and 12 positions in glycerol monolinoleate as shown in Figure 6 plus the –OH in the glycerol make it very difficult for glycerol monolinoleate to fit into the central opening of the urea crystal.

The photographs illustrate the reason for greater stability of the glycerol monostearate adduct as compared with that of the monoester of the unsaturated acids. The position of the monoester in the photograph shows the maximum deviation from linearity that the double bonds can create in the molecule. There are an infinite number of other positions that are closer to a linear arrangement of the saturated acid, but, regardless of what position the fatty acid chain takes to appear more linear, the dimensions around the double bond cannot be made smaller and it is this dimension that must be fitted into the lumen of the urea crystal. The models are made to a scale on which 1 centimeter equals 1 Å, so it is possible to measure the cross-section diameter at the double bond and at the glycerol end of the ester. The diameter of the cross-section of the monoester at the hydroxyl group is about 5.4 Å. Since the opening in the urea crystal is 5.5-6.0 Å, the hydroxyl part could hinder complex formation, but since it occurs at the end of the chain, it is possible for the complex to be stabilized by adduct formation with the long fatty acid chain. Diameter of the cross-section of the stearic acid part is about 4.1 Å. This is the ideal size for maximum stability. Diameter of the oleic acid at the *cis* double bond in the 9 position is about 5.0 Å. This extra width makes its complex with urea less stable than the urea-stearic acid monoglyceride complex. Diameter of the linoleic acid at the two *cis* double bonds in the 9 and 12 positions is about 5.4 Å. This means that both the hydroxyl groups and the 9 and 12 double bonds are sufficiently large to create stresses in the urea crystal latice. Results obtained indicate that the urea crystal is so strained that the urea-glycerol monolinoleate complex does not form readily in mixture with oleic and stearic acid monoglyceride. Diameter of the *cis* double bonds in linolenic acid is about 5.7 Å, making it almost impossible for urea to form a complex with glycerol monolinolenate.

Swern, Witnauer, and Knight (9) have shown that high-melting dihydroxystearic acid (m.p. 131°C.) will not form an adduct because it has a calculated cross-section diameter of 6.0 Å. This is about the size of the central opening of the urea spiral crystal. Swern *et al.* have also shown that low-melting dihydroxystearic acid (m.p. 95°C.) with a calculated cross-section diameter of 5.4 Å will form an adduct with urea. This might indicate that glycerol monolinoleate can form an adduct with urea. However the fact that both the glycerol part and the two *cis* double bonds increase the cross-section diameter of the molecule to 5.4 Å may account for the fact that the monolinoleate did not readily form an adduct with urea in the extractions reported here.

Urea Extraction of Soybean Oil Monoglycerides. Fifty g. of distilled soybean oil monoglycerides (sa-

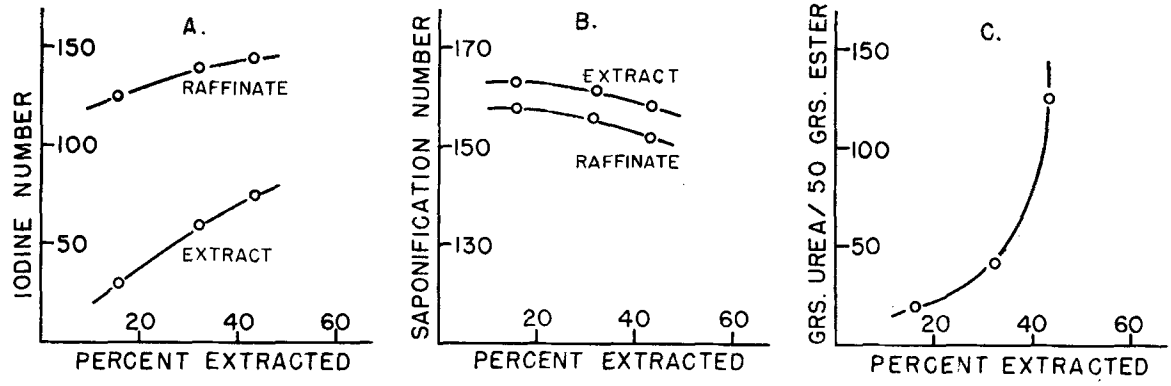

FIG. 2. Urea extraction of glycerol monoester of soybean oil fatty acids (saponification number 154, iodine number 109).

ponification number 154, iodine number 109) were extracted with 20, 42, and 125 g. of urea. Amounts in the six fractions, iodine and saponification numbers of the fractions, are shown in Figures 2A, 2B, and 2C. The 125 g. of urea extracted 20.85 g., or 42% of the 50 g. of soybean monoester in the extraction batch. The 125 g. of urea should have extracted 40-42 g. of the monoester. The shape of the curve in Figure 2C shows that additional urea would not increase the amount that would be extracted. The iodine number of extract and raffinate, using 125 g. of urea, was 74 and 142 while that of glyceryl mono-oleate and monolinoleate were 76 and 144. These values indicate that the extract contains principally glyceryl mono-oleate while the raffinate contains principally glycerol monolinoleate with about equal parts of glycerol mono-oleate and monolinolenate. The separation is not exact for there are some oleic esters in the raffinate and linoleate esters in the extract. Saponification values of the extracts were consistently higher than those of the raffinate, indicating that the 7% of glycerol monopalmitate with a saponification number of 170 was contained in the extract. Saponification number for glycerol monostearate is 157 and for glycerol monolinoleate is 159.

Urea Extraction of Technical Glycerol Monolaurate. A sample of technical glycerol monolaurate (saponification number 202) containing approximately 40% monolaurate was washed with a 20% Na_2SO_4 solution to remove unreacted glycerol. Approximately 10% was removed by washing. After washing, the glyceride mixture had a saponification number of 222. One hundred grams of the washed glycerol monolaurate were dissolved in 200 g. of methyl isobutyl ketone and extracted with 70 g. of crystalline urea. The 70 g. of urea extracted 28.33 g., or 28% of glycerol monolaurate. Saponification number of the 28% extract was 214 and that of the raffinate fraction was 227.

If there are only small amounts of other fatty acid glycerides in the monolaurate, saponification numbers could be used to measure the amount of mono- and diester present. Glycerol monolaurate has a saponification number of 246. On this basis the technical mixture of glycerol monolaurate contained 60% monoester. Also on this same basis, the extract with a saponification number of 214 contains about 78% monolaurate, and the raffinate with a saponification number of 227 contained 46% monoester. Since all the esters are saturated esters, urea has formed a complex on the basis of whether the monoglyceride or diglyceride was more linear. Results indicate that the urea-glycerol monoester complex is more stable and forms at a faster rate than does the urea-glycerol diester. In one case the hydroxyl group is in the middle between the long chains; in the other urea forms an adduct with the single chain, and the two hydroxyl groups on the short glycerol chain do not make the adduct unstable. It is assumed that in glycerolysis of the oil the diesters formed are predominantly the alpha isomers.

Urea Extractions of 50-50 Mixtures of Glycerol Mono- and Diesters of Cottonseed Fatty Acids. The 50-50 mixtures of cottonseed oil fatty acid monoesters and diesters were made by mixing equal parts of cottonseed oil monoglycerides (saponification number 159, iodine number 94) and cottonseed oil diglycer-

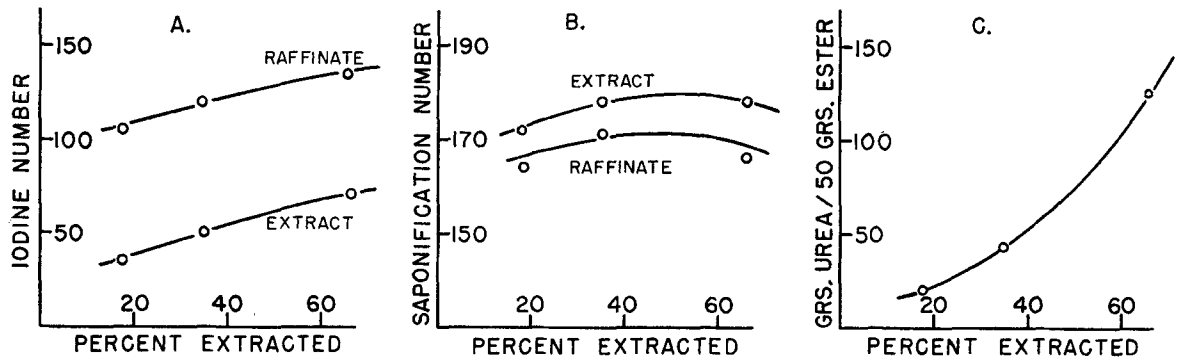

FIG. 3. Urea extraction of a 50-50 mixture of glycerol mono- and diester of cottonseed oil fatty acids (saponification number 171, iodine number 96).

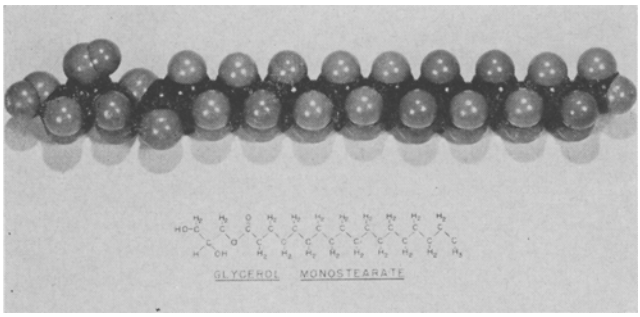

FIG. 4. Glycerol monostearate (forms a urea adduct).

ides (saponification number 183, iodine number 97). Fifty-gram samples of this mixture were extracted with 20, 42, and 125 g. of urea.

Twenty grams of urea extracted 8.72 g., or 17% of the mixture of di- and monoester. The iodine number of the 17% extract was 35, and that of the raffinate fraction was 107. The spread in iodine number between the two fractions was 72, not quite as great as that obtained with the same amount of urea with distilled monoglyceride. Saponification number of the extract was 173 while that of the raffinate was 164. Closeness of the saponification numbers indicates that the urea has not separated monoesters from the diesters to a significant degree.

Mono- and diester content cannot be accurately determined by the saponification number in a mixture such as this. The diglycerides of cottonseed oil fatty acids will not occur as dipalmitates, distearates, dioleates, etc., but will be mixed glycerides. Instead of glycerol dipalmitate being extracted first to give extracts with saponification numbers of 197, the extracted material will more likely be a diglyceride of palmitic and oleic acid which would have a saponification number of approximately 188. If urea forms a complex with monoesters, saponification number 164, as easily as it does with diesters, the extract would be a mixture of the two and have a saponification number of around 176.

Results of these three extractions indicate that this is approximately what has happened. Urea indiscriminately has formed a solid complex with mono- and diglycerides on the basis of saturation only. As long as there is a saturated or oleic acid on the ester molecule, whether mono- or diester, urea forms a solid complex with it.

Forty-two g. of urea extracted 17.10 g., or 34% of the 50 g. of cottonseed oil mono- and diglycerides.

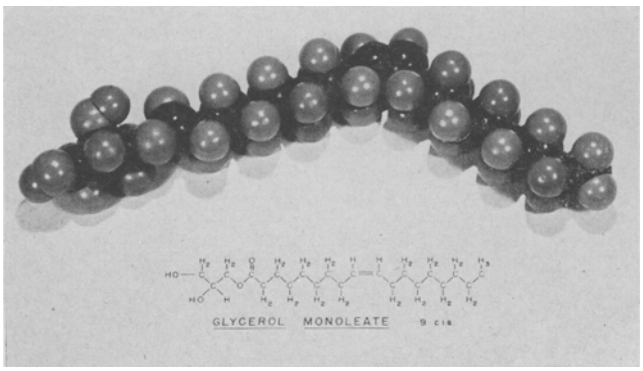

FIG. 5. Glycerol mono-oleate (forms a urea adduct).

The iodine number and saponification number of the extract were 49 and 177. The iodine number and saponification number of the raffinate fraction were 118 and 171. The iodine number spread between the two fractions was 69, but spread in saponification number was only 6 numbers. Urea separated the mixture principally along lines of saturation, not on the basis of mono- and diester.

Some 125 g. of urea extracted 32.40 g. of the mixture of mono- and diesters, or 65% of the 50 g. of esters present in the batch. In the case of monoglycerides, urea formed a complex with only 48% of the monoesters present. Larger extraction with diesters arises from the random distribution of the fatty acids on the diglyceride molecule. Because the diglyceride is a mixed glyceride of stearic and linoleic acids, the urea-fatty acid complex will be less stable due to the stress placed on the urea crystal by the size and shape of the linoleic acid; however the complex with the diglyceride gains sufficient stability from the stearic acid part and so the diglyceride is extracted intact. Esterification of the third hydroxyl group gives a branched chain molecule that cannot form a complex with urea.

Urea Extraction of a Technical Glycerol Monooleate. A sample of a technical glycerol mono-oleate containing 40% monoester, saponification number 162,

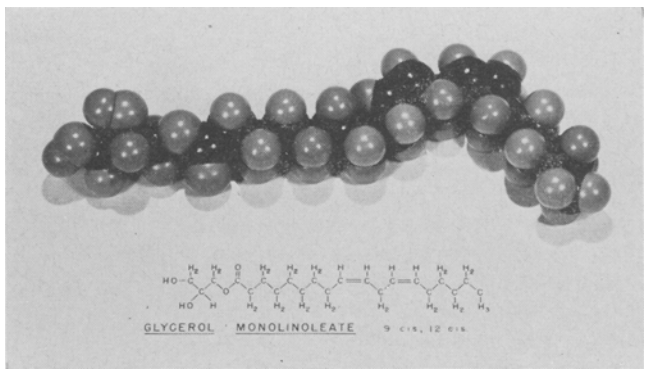

FIG. 6. Glycerol monolinoleate (will not readily form an adduct with urea).

was washed with 20% solution of Na_2SO_4 to remove free glycerin. Approximately 8% of the technical monoglyceride was removed by washing. Two hundred g. of the washed product (saponification number 170 and iodine number 84) were dissolved in 300 g. of methyl isobutyl ketone and extracted with 250 g. of urea. The 250 g. of urea extracted 72.4 g., or 36% of the glyceride mixture. Iodine and saponification numbers of the extract were 66 and 170. The raffinate fraction amounting to 58% had an iodine number of 94 and a saponification number of 171.

Technical monoglycerides contain almost as many diglycerides as monoglycerides. The presence of the dioleate and distearate glyceride accounts for the high saponification number of 170 for the technical mixture. The extract and raffinate after extraction had a saponification number of 170 and 171, indicating that the urea did not separate the mono- and diesters. If a diglyceride had been concentrated in the raffinate, the saponification number of it would have been 10 points higher. Iodine number of extract was 66, and that of the raffinate was 94. Urea extrac-

tion of the technical monoglyceride mixture has concentrated in the extract the mono- and diesters of stearic acid present in the reaction mixture. The spread in iodine number of the two fractions was 28. The spread in iodine number would have been greater at a smaller amount extracted, or if there had been fewer diglycerides of mixed acids in the mixture.

Summary

The experimental work has shown how molecular configurations of fatty acid glycerides affect urea complex formation. Extraction data indicate that urea will form a complex with glycerol monopalmitate, monostearate, and mono-oleate but not under these conditions with glycerol monolinoleate or monolinolenate from mixtures containing these monoesters. Data also indicate that it is easier for urea to form a complex with monoglycerides than with diglycerides. In a mixture containing mono- and diglycerides of saturated and unsaturated fatty acids, urea will separate first on the basis of saturation, then secondly on the basis of the degree of esterification of the glycerol.

REFERENCES

1. Kuhrt, N. H., Welch, Eileen A., and Kovarick, F. J., J. Am. Oil Chemists' Soc., *27*, 310-313 (1950).
2. Kuhrt, N. H., and Welch, Eileen A., J. Am. Oil Chemists' Soc., *27*, 344 (1950).
3. Detwiler, S. B., Bull, W. C., and Wheeler, D. H., Oil and Soap, *20*, 108 (1943).
4. Feuge, R. V., and Gros, Audrey T., J. Am. Oil Chemists' Soc., *27*, 117 (1950).
5. Newey, H. A., Shokal, E. C., Mueller, A. C., Bradley, T. F., and Fetterly, L. C., Ind. and Eng. Chem., *72*, 2538-41 (1950).
6. Swern, Daniel, and Parker, W. E., J. Am. Oil Chemists' Soc., *29*, 431-34, 614-15 (1952); *30*, 5-7 (1953).
7. Fetterly, L. C., Ph.D. Thesis, University of Washington (1950).
8. Schlenk, H., and Holman, R. T., J. Am. Chem. Soc., *72*, 5001-4 (1950).
9. Swern, Daniel, Witnauer, L. P., and Knight, H. B., J. Am. Chem. Soc., *74*, 1655 (1952).

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Composition of Liver Fats of Mature and Embryo Sharks (Galeocerdo tigrinus)

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THE EXCEPTIONALLY high contents of saturated acids in the liver fats from some Asiatic species of Elasmobranch fish (including sharks) have been observed by Tsujimoto (11, 12, 13) and by Wang and Kan (14). More recent studies conducted in this laboratory (8, 9, 10) have shown that the high content of saturated acids (*ca.* 40%) is characteristic of a group of Elasmobranch fish.

The present communication reports the comparative composition of the liver fats of mature and embryo sharks *(Galeocerdo tigrinus)*. Both contained about 40% of saturated acids.

Experimental

Two specimens of livers were supplied by the Government Oil Factory, Kozhikode, Calicut, Madras, from sharks caught in the Bay of Bengal. The first, designated as No. 1, was from the liver of a mother shark (120 in. in length). It weighed 49 lbs. and yielded 30% fat having a vitamin A potency of 9,970 i.u./g. The second specimen (No. 2) consisted of the livers of 12 male and 6 female embryo sharks (approximately 21 in. in length). The total weight of the embryo shark livers was 11 lbs. and yielded 45.5% fat having a vitamin A potency of 410 i.u./g.

Fat No. 1. A yield of 167 g. of mixed fatty acids (I. V. 88.5) was obtained from 180 g. of the phosphatide free oil on saponification and removal of the unsaponifiable matter. These mixed acids were fractionated into three groups of varying unsaturation by the lithium (13) and lead salt alcohol (1) methods: (A) 71.0 g. (I.V. 9.5); (B) 64.0 g. (I.V. 132.1); and (C) 32.0 g. (I.V. 146.3).

Each fraction of the acids was esterified with methyl alcohol, and the esters were fractionated by use of the E.H.P. column (Longenecker's) (2) in the usual manner (8).

The composition of the mixed fatty acids (Table I) was calculated from the saponification equivalents and iodine values of the ester fractions by the method described by Hilditch (1). The mean equivalent of each homologous ester group was found by interpolation and extrapolation of the unsaturation of each fraction.

Fat No. 2. The lead salt ether method (1) was used to fractionate 186.0 g. of the mixed acids (I.V. 57.7), obtained as described for Fat No. 1, into two fractions: (A) 70.0 g. (I.V. 3.3) and (B) 116.0 g. The composition of the mixed fatty acids is given in Table II.

TABLE I

Fat No. 1: Component Acids in Groups A, B, and C and Total Fatty Acids (all values as percentages of total)

Acids	A (42.5%)	B (38.3%)	C (19.2%)	Total (100.0%)
	%	%	%	%
Myristic	2.43	0.54	.....	2.97
Palmitic	23.46	1.67	.....	25.13
Stearic	13.06	0.76	.....	13.82
Arachidic	1.32	.....	.....	1.32
Unsaturated				
C_{14}	.....	0.43(−2.0)	.....	0.43(−2.0)
C_{16}	0.36(−2.0)	6.35(−2.0)	1.10(−2.0)	7.81(−2.0)
C_{18}	1.28(−2.0)	18.43(−4.0)	3.91(−4.0)	23.62(−2.6)
C_{20}	0.54(−2.0)	10.07(−5.1)	4.91(−6.8)	15.52(−5.6)
C_{22}	.....	.....	9.26(−10.5)	9.26(−10.5)
Unsaponifiables	0.05	0.05	0.02	0.12

TABLE II

Fat No. 2: Component Acids in Groups A and B and Total Fatty Acids (all values as percentages of total)

Acids	A (37.63%)	B (62.37%)	Total (100.0%)
	%	%	%
Myristic	8.51	0.06	8.57
Palmitic	23.20	1.93	25.13
Stearic	4.32	0.73	5.05
Unsaturated			
C_{14}	0.16(−2.0)	0.07(−2.0)	0.23(−2.0)
C_{16}	0.70(−2.0)	17.25(−2.0)	17.95(−2.0)
C_{18}	0.53(−2.0)	37.71(−2.1)	38.24(−2.1)
C_{20}	.....	3.94(−4.4)	3.94(−4.4)
Unsaponifiables	0.21	0.68	0.89